



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Johannes Wilhelmus Maria Sonnemans, et al.

: Docket: ACH 2823US

: Examiner: Tam M Nguyen

Serial No.: 942,830

: Group Art Unit: 1764

Filing Date: August 30, 2001

For: PROCESS FOR EFFECTING ULTRA DEEP:
HDS OF HYDROCARBON FEEDSTOCKS :

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Commissioner of Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Enclosed herewith is a certified copy of European Patent Application No.
00203078.1, filed on September 4, 2000.

Respectfully submitted,

Louis A. Morris
Attorney for Applicants
Reg. No. 28,100

Akzo Nobel Inc.
Intellectual Property Department
7 Livingstone Avenue
Dobbs Ferry, New York 10522-3408
(312) 544-7378

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as First-Class
Mail in an envelope addressed to the Commissioner of Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450 on:

August 18, 2004

Vickie Purcell

THIS PAGE BLANK (USPTO)



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00203078.1

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 08/10/01
LA HAYE, LE

THIS PAGE BLANK (USPTO)



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°: 00203078.1

Anmeldetag:
Date of filing: 04/09/00
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
Akzo Nobel N.V.
6824 BM Arnhem
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Process for effecting ultra-deep hds of hydrocarbon feedstocks

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

C10G45/08, C10G65/04

Am Anmeldetag benannte Vertragsstaaten:

Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

THIS PAGE BLANK (USPTO)

EPO - DG 1

04. 09. 2000

ACH 2823 PDEP

PROCESS FOR EFFECTING ULTRA-DEEP HDS OF HYDROCARBON FEEDSTOCKS

5

The present invention relates to a process for effecting ultra-deep HDS of hydrocarbon feedstocks.

10

In an effort to regulate SO₂ emissions from the burning of fuels and to optimise the performance of tail-end catalysts, in particular exhaust treatment catalysts, the regulations as to the sulphur content of fuels, in particular diesel fuels, are becoming more and more strict. In Europe as of 2000 diesel feedstocks will be required to have a sulphur content below 350 ppm, while as of 2005, the sulphur content should be below 50 ppm, with even further decreases not being excluded.

15

In consequence, there is an increasing need for catalyst systems which can decrease the sulphur content of a hydrocarbon feedstock with a 95% boiling point of 450°C or less to below 200 ppm, preferably below 100 ppm, even more preferably below 50 ppm, calculated by weight as elemental sulphur on the total liquid product.

20

In the context of the present specification the term ultra-deep HDS means the reduction of the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm, preferably less than 100 ppm, and even more preferably to a value of less than 50 ppm, calculated by weight as elemental sulphur on the total liquid product, as determined in accordance with ASTM D-4294. The indications Group VIB and Group

25

VIII correspond to the Periodic Table of Elements applied by Chemical Abstract Services (CAS system).

The problem associated with effecting this ultra-deep HDS is that the only sulphur compounds still present in the feed are those which are very difficult to remove.

30

Depending on their source, petroleum fractions can comprise various types of sulphur compounds. In hydrotreated middle distillate fractions, the major sulphur components are benzothiophenes and dibenzothiophenes. In straight-run materials significant quantities of other components are present, such as thiophenes, mercaptanes, sulphides, and disulphides. Of these, the sulphides and disulphides are the most

35

reactive, followed by the thiophenes, benzothiophenes, and dibenzothiophenes. Within

ACH 2823 PDEP

2

the group of dibenzothiophenes some components are more reactive than others. In consequence, in conventional HDS, in which the sulphur level is reduced to a value of, say, about 0.3 wt.%, the sulphides and thiophenes are removed. In deep HDS, to a sulphur level of, say, 200-500 ppm, the benzothiophenes are removed. The only
5 compounds remaining then are a limited number of alkylated benzothiophenes, with the alkylidibenzothiophenes which have the alkyl on the 4- or 6- position being particularly difficult to remove.

It has also been found that the reaction mechanisms by which these very refractive
10 sulphur compounds are decomposed is different from those by which the less refractive compounds are decomposed. This is evidenced, e.g., by the fact that the catalysts which are known as particularly suitable for HDS appear to function less well in ultra-deep HDS. For example, conventionally cobalt-molybdenum catalysts are more active in HDS than nickel-molybdenum catalysts. However, for ultra-deep HDS it has
15 been found that nickel-molybdenum catalysts show better results than cobalt-molybdenum catalysts. Reference is made to the paper entitled "Ultra low sulphur diesel: Catalyst and Process options" presented at the 1999 NPRA meeting by T. Tippet et al.

20 The consequence of this difference in reaction mechanisms implies that the refiner who is faced with having to produce material with a lower sulphur content cannot just apply his usual hydrodesulphurisation catalyst under more stringent conditions. On the contrary, he will have to specifically select the hydrotreating catalyst which is most effective in effecting ultra-deep HDS. This is the more so since the reaction conditions
25 necessary to effect ultra-deep HDS are rather severe in themselves, and the use of a better catalyst makes it possible to select less severe reaction conditions, resulting in energy saving and a longer catalyst lifespan.

We have now found that a catalyst which comprises a Group VIB metal component, a
30 Group VIII metal component, and an S-containing organic additive is particularly efficient in reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm. Additionally, it has appeared that this catalyst makes it possible to effect ultra-deep HDS in combination with improved nitrogen removal, total aromatics removal, and removal of polynuclear aromatics.

ACH 2823 PDEP

3

Therefore, the present invention is directed to a process for reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive on a carrier to a sulphidation
5 step or activation step, and contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 500 ppm or less with the optionally sulphided or activated sulphided catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.

10 The additive-containing catalyst

In principle, the additive-containing catalyst can be any catalyst which comprises a Group VIB hydrogenation metal and/or a Group VIII hydrogenation metal, and an S-containing organic additive on a carrier. Catalysts comprising the combination of a
15 Group VIB hydrogenation metal and a Group VIII hydrogenation metal are preferred.

Catalysts which comprise a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive are known in themselves in the art.

For example, European patent application No. 0 300 629 and European patent application No. 0 357 295 describe hydrotreating catalysts comprising a support
20 impregnated with at least one member of molybdenum, tungsten, and/or metals of Group VIII of the Periodic Table, and a mercapto-compound selected from mercaptocarboxylic acids, amino-substituted mercaptanes, di-mercaptanes, and thioacids. The S-containing additive is incorporated into the catalyst composition to obviate the necessity of presulphiding, or to at least make the presulphiding less
25 difficult.

European patent application No. 0 506 206 also describes a hydrotreating catalyst comprising an S-containing additive selected from the group of bi-mercaptanes, aminosubstituted mercaptanes, and thiocarboxylic acids. The S-containing catalyst is again intended to avoid the necessity of presulphiding. Some of the catalysts
30 described in this reference are activated by a treatment with hydrogen at a temperature from room temperature up to 400°C, preferably 100-300°C.

Similar subject-matter is described in European patent application No. 0 338 788, and European patent application No. 0 289 211.

ACH 2823 PDEP

4

US 5,139,990 describes a hydrotreating catalyst comprising a carrier and hydrogenation metal components which is treated with an aqueous medium comprising a water-soluble or water-miscible S-containing organic additive, followed by drying the resulting catalyst and activating it with hydrogen at a temperature of 100-600°C.

- 5 US 4,636,487 describes a hydrotreating catalyst comprising a support and a hydroxymercaptide of one or more metals, which may be the reaction product of a mercaptoalcohol and one or more metal compounds. The catalyst may be activated with hydrogen at a temperature of 66-316°C.

- 10 European patent application No. 0 496 592 describes a hydrotreating catalyst comprising a carboxylic acid and an organic sulphur compound which may be a mercaptocarboxylic acid.

- As Group VIB metals suitable for use in the additive-containing catalyst for use in the process according to the invention may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. Catalysts comprising molybdenum as Group VIB metal component and nickel and/or cobalt as Group VIII metal component are the most common. The catalyst usually has a metal content in the range of 0.1 to 50 wt.% calculated as oxides on the dry weight of the catalyst not containing the additive. The Group VIB metal will frequently be present in an amount of 15 5-40 wt.%, preferably 15-30 wt.%, calculated as trioxide. The Group VIII metal will frequently be present in an amount of 1-10 wt.%, preferably 2-7 wt.%, calculated as monoxide. The catalyst may also contain other components, such as phosphorus, halogens, and boron. Particularly, the presence of phosphorus in an amount of 1-10 wt.%, calculated as P_2O_5 , may be preferred.

- 25 The catalyst carrier may comprise the conventional oxides, e.g., alumina, silica, silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and titania, as well as mixtures of these oxides. As a rule, preference is given to the carrier comprising alumina, silica-alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given 30 to the carrier consisting essentially of alumina or alumina containing up to 25 wt.% of other components, preferably silica. A carrier comprising a transition alumina, for example an eta, theta, or gamma alumina is preferred within this group, with a gamma-alumina carrier being especially preferred. Additionally, although it is considered less preferred at present, the catalyst may contain 0-60 wt.% of zeolite.

The catalyst's pore volume (measured via N2 adsorption)) generally is in the range of 0.25 to 1 ml/g. The specific surface area will generally be in the range of 50 to 400 m²/g (measured using the BET method). Generally, the catalyst will have a median pore diameter in the range of 7-20 nm, as determined by N2 adsorption. The figures for the pore size distribution and the surface area given above are determined after calcination of the catalyst at 500°C for one hour.

The catalyst is suitably in the form of spheres, pellets, beads, or extrudates. Examples of suitable types of extrudates have been disclosed in the literature (see, *int. al.*, US 4,028,227). Highly suitable are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles (3 or 4 lobes).

The additive present in the catalyst may be any S-containing organic additive. In the context of the present specification the term organic additive refers to an additive comprising at least one carbon atom and at least one hydrogen atom.

Preferred compounds include the mercaptocarboxylic acids represented by the general formula HS-R1-COOR, wherein R1 stands for a divalent hydrocarbon group with 1-10 carbon atoms and R stands for a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, or a linear or branched alkyl group having 1 to 10 carbon atoms. Examples include mercaptoacetic acid (HS-CH₂-COOH), beta-mercaptopropionic acid (HS-CH₂CH₂-COOH), methylmercaptoacetate (HS-CH₂-COOCH₃), ethyl 2-mercaptoacetate (HS-CH₂-COOC₂H₅), ethylhexyl mercaptoacetate (HS-CH₂-COOC₈H₁₇), and methyl 3-mercaptopropionate (HS-CH₂CH₂-COOCH₃).

Preferred compounds also include amino-substituted mercaptanes represented by the general formula H₂N-R₂-SH, wherein R₂ stands for a divalent hydrocarbon group having 1-15 carbon atoms. Examples of these compounds include 2-amino ethanethiol (H₂N-CH₂CH₂-SH), and 4-amino thiophenol (H₂N-C₆H₄-SH).

Preferred compounds also include di-mercaptanes represented by the general formula HS-R₃-SH, wherein R₃ stands for a divalent hydrocarbon group having 1-15 carbon atoms. Examples of these compounds include ethanedithiol (HS-CH₂CH₂-SH) and 1,4-butanedithiol (HS-(CH₂)₄-SH).

Preferred compounds also include thioacids of the formula R₄-COSH, wherein R₄ stands for a monovalent hydrocarbon group having 1-15 carbon atoms. Examples of these compounds include thioacetic acid (CH₃-COSH) and thiobenzoic acid (C₆H₅COSH). Dithioacids of the formula HSOC-R₅-COSH wherein R₅ is a divalent

hydrocarbon group with 1-15 carbon atoms may also be suitable. An example is dithioadipic acid ($\text{HSOC-C}_4\text{H}_{10}\text{-COSH}$).

Preferred compounds also include mercaptoalcohols of the general formula $\text{R}_6\text{S-R}_5\text{-(OH)}_n$, wherein R_5 represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group, R_6 represents a hydrogen atom or an alkyl group having 1 or 2 carbon atoms, and n is 1 or 2. Examples of these compounds include 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercaptophenol, 2-(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2-propanediol, 3-methylthio-1,2, propanediol, and 3-ethylthio-1,2, propanediol.

Other suitable compounds include sulfoxides of the formula $\text{R}_7\text{-SO-R}_8$, wherein R_7 and R_8 are hydrocarbon groups with 1-5 carbon atoms. An example is dimethyl sulfoxide ($\text{CH}_3\text{-SO-CH}_3$).

Ammonium thiocyanate and thiourea may also be useful compounds, as may be the various dithiocarbamic acids and the salts thereof, such as ethylene bisdithiocarbamic acid and its salts, and dimethyl dithiocarbamic acid and its salts. Other suitable compounds include mercaptodiathiazoles and their salts, such as 2,5-dimercapto-1,3,4,-diathiazoles and its salts.

Other compounds which may be useful are polysulphides of the formula $\text{R}_9\text{-S}_x\text{-R}_{10}$, wherein x is a value of 1-15 and R_9 and R_{10} are alkyl groups, preferably branched alkyl groups, with 1-30 carbon atoms. Related compounds are those with the formula $\text{HO-R}_{11}\text{-S}_x\text{-R}_{12}\text{-OH}$, wherein x is a value of 1-15 and R_{11} and R_{12} are alkyl groups with 1-8 carbon atoms.

At this point in time the mercaptocarboxylic acids are considered preferred for reasons of activity. Other compounds, in particularly those which are soluble in or miscible with water, may be preferred for environmental reasons (less odour and/or no organic solvent necessary).

A single compound as well as a combination of compounds may be used as additive.

The amount of additive present in the additive-containing catalyst depends on the specific situation. It was found that the appropriate amount of additive generally lies in the range of 0.01-2.5 moles of additive per mole of hydrogenation metals present in the catalyst. If the amount of additive added is too low, the advantageous effect associated with its presence will not be obtained. On the other hand, the presence of an exceptionally large amount of additive will not improve its effect. Generally, the aim

is to select the amount of sulphur incorporated into the catalyst by way of the additive to correspond to 5-200%, preferably 50-200%, more preferably 80-150%, of the stoichiometric sulphur quantity necessary to convert the hydrogenation metals into Co_9S_8 , MoS_2 , WS_2 , and Ni_3S_2 , respectively.

5

The way in which the additive is incorporated into the catalyst composition is not critical to the process according to the invention. The additive may be incorporated into the catalyst composition prior to, subsequent to, or simultaneously with the incorporation of the hydrogenation metal components.

10 For example, the additive can be incorporated into the catalyst composition prior to the hydrogenation metal components by being added to the carrier before the hydrogenation metal components are. This can be done by mixing the additive with the carrier material before it is shaped, or by impregnating the shaped carrier material with the additive. This embodiment is not preferred at this point in time.

15 Alternatively, the additive can be incorporated into the catalyst composition simultaneously with the hydrogenation metal components. This can be done, e.g., by mixing the additive and the hydrogenation metal components with the carrier material before shaping or by impregnating the carrier with an impregnation solution comprising the hydrogenation metal components and the additive, followed by drying under such
20 conditions that at least part of the additive is maintained in the catalyst.

It is also possible to incorporate the additive into the catalyst composition subsequent to the hydrogenation metal components. This can be done, e.g., by first incorporating the hydrogenation metal components into the catalyst composition, e.g., by mixing them with the carrier material or by impregnating the carrier with them, optionally
25 followed by drying and/or calcining, and subsequently incorporating the additive, e.g., by impregnation.

Depending on the nature of the additive and the way in which it is incorporated into the catalyst composition, the additive may be used in the solid form, in the liquid form, or dissolved in a suitable solvent. It may be preferred for the additive to be incorporated
30 into the catalyst dissolved in water.

The catalyst may be activated by contacting it with hydrogen at a temperature of 100-600°C as described in, e.g., EP 0 506 206, EP 0 338 788, EP 0 289 211, US 4,636,487, and US 5,139,990. Optionally, the catalyst may be contacted with an

organic liquid either prior to or simultaneously with the contacting with hydrogen. Such a process is the subject of non-prepublished European patent application No. 00201294 filed on April 11, 2000, which is incorporated herein by reference.

- 5 If so desired, the catalyst may be subjected to a sulphiding step before its use in effecting ultra-deep HDS, said sulphiding step taking place *ex situ*, *in situ* or in a combination of *ex situ* and *in situ*. In the context of the present specification, the indication sulphiding step or sulphidation step is meant to include any process step in which a sulphur-containing compound is added to the catalyst composition and in
10 which at least a portion of the hydrogenation metal components present in the catalyst is converted into the sulphidic form, either directly or after an activation treatment with hydrogen.

Suitable sulphidation processes are known in the art. *Ex situ* sulphidation processes take place outside the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. In such a process the catalyst is contacted with a sulphur
15 compound, e.g. a polysulphide or elemental sulphur, outside the reactor and, if necessary, dried. In a second step, the material is treated with hydrogen gas at elevated temperature in the reactor, optionally in the presence of a feed, to activate the catalyst, i.e. bring it into the sulphided state.

- 20 *In situ* sulphidation processes take place in the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. Here, the catalyst is contacted in the reactor at elevated temperature with a hydrogen gas stream mixed with a sulphiding agent, such as hydrogen sulphide or a compound which under the prevailing conditions is decomposable into hydrogen sulphide. It is also possible to use a hydrogen gas
25 stream combined with a hydrocarbon feed comprising a sulphur compound which under the prevailing conditions is decomposable into hydrogen sulphide. In the latter case it is possible to use a hydrocarbon feed comprising an added sulphiding agent (a so-called spiked feed), but it is also possible to use a sulphur-containing hydrocarbon feed without any added sulphiding agent, since the sulphur components present in the
30 feed will be converted into hydrogen sulphide in the presence of the catalyst. The hydrocarbon feed may be the feed to be subjected to ultra-deep HDS in the process according to the invention, but it may also be a different feed, later to be replaced with the feed to be subjected to ultra-deep HDS. Combinations of the various sulphiding techniques may also be applied. In the context of the present invention it may be

preferred to sulphide the catalyst by contacting it with an, optionally spiked, hydrocarbon feed.

A further process for presulphiding catalysts comprising an organic S-containing catalyst is the subject of non-prepublished European patent application No. 00201299,
5 filed on April 11, 2000, which is incorporated herein by reference. This patent application is directed to a presulphiding process in which a catalyst comprising a sulphur-containing additive is contacted with hydrogen and a sulphur-containing compound in the gaseous phase.

Another process, which may be preferred over the one of non-prepublished European
10 patent application No. 00201299 mentioned above, is the one described in non-prepublished European patent application No. 00201295, filed on April 11, 2000, which is also incorporated herein by reference. This patent application is directed to a presulphiding process in which a catalyst comprising a sulphur-containing additive is first contacted with an organic liquid followed by being contacted with hydrogen and a
15 sulphur-containing compound in the gaseous phase.

The feed

The feedstock suitable for use in the process according to the invention has a 95%
20 boiling point, as determined in accordance with ASTM D-2887, of 450°C or less, preferably 420°C or less, more preferably 400°C or less. That is, 95 vol.% of the feedstock boils at a temperature of 450°C or less, preferably 420°C or less, more preferably 400°C or less. Generally, the initial boiling point of the feedstock is above 100°C, preferably above 180°C. The feed contains less than 500 ppm of sulphur,
25 preferably 150-500 ppm of sulphur.

The feedstock to be used in the process according to the invention may be prepared by hydrodesulphurisation of starting hydrocarbon feedstocks containing 0.1 wt.% or more of sulphur, preferably 0.2 to 3.5 wt.% of sulphur, more preferably 0.5 to 2.0 wt.%
30 of sulphur. This starting feedstock generally has a 95% boiling point, as determined in accordance with ASTM D-2887, of 450°C or less, preferably 420°C or less, more preferably 400°C or less. Generally, the initial boiling point of the feedstock is above 100°C, preferably above 180°C. The feedstock generally contains 20-1200 ppm nitrogen, preferably 30-800 ppm, more preferably 70-600 ppm. The metal content of

the feedstock preferably is less than 5 ppm, more preferably less than 1 ppm (Ni+V). Examples of suitable starting feedstocks are feedstocks comprising one or more of straight run gas oil, light catalytically cracked gas oil, and light thermally cracked gas oil, and (mild) hydrocracked oils.

- 5 The above-mentioned starting hydrocarbon feedstock is subjected to hydrodesulphurisation to reduce its sulphur content to a value below 500 ppm. This hydrodesulphurisation process can be carried out using conventional hydrodesulphurisation catalysts comprising a Group VIB metal component, a Group VIII metal component, and, optionally, phosphorus on a carrier comprising alumina.
- 10 Suitable hydrodesulphurisation catalysts are commercially available, and include for example KF 756 and KF 901 of Akzo Nobel. It is also possible to obtain the feedstock for the process according to the invention from a starting feedstock containing more sulphur by means of a two-step process, such as those described in EP 0 464 931, EP-A 0 523 679 or EP 870 807.

15

- Additionally, it is also possible to obtain the feedstock for the process of the invention from the above-mentioned starting feedstock by using an additive-based catalyst. The present invention thus also relates to a two-step process for converting a starting feedstock having a sulphur content of above 0.1 wt.% into a product having a sulphur
- 20 content of 200 ppm or less, wherein the process comprises sulphidation of a first and a second catalyst comprising a Group VIB metal component, a Group VIII metal component, and an organic additive on a carrier, contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 0.1 wt.% or more with the first sulphided catalyst under conditions of elevated temperature and pressure to form a
- 25 product with a sulphur content of less than 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, optionally including removal of H₂S and NH₃ formed, with the second sulphided catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.
- 30 In this process, the first and second catalysts containing an organic additive before sulphidation may be the same or different. It is considered preferred at this point in time for the first catalyst to comprise molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, with the second catalyst comprising molybdenum as Group VIB metal component and nickel as Group VIII

metal component. The two-step process can be carried out in one or two reactors, as may be desired.

The process conditions

5

The process according to the invention is carried out at elevated temperature and pressure. The temperature generally is 200-450°C, preferably 280-430°C. The reactor inlet hydrogen partial pressure generally is 5-200 bar, preferably 10-100 bar, more preferably 15-60 bar. The liquid hourly space velocity preferably is between 0.1 and 10 vol./vol.h, more preferably between 0.5 and 4 vol./vol.h. The H₂/oil ratio generally is in the range of 50-2000 NI/I, preferably in the range of 80-1000 NI/I.

The process conditions are selected in such a way that the sulphur content of the total liquid effluent is less than 200 ppm, preferably less than 100 ppm, more preferably less than 50 ppm. The exact process conditions will depend, int. al., on the nature of the feedstock, the desired degree of hydrodesulphurisation, and the nature of the catalyst. In general, a higher temperature, a higher hydrogen partial pressure, and a lower space velocity will decrease the sulphur content of the final product. The selection of the appropriate process conditions to obtain the desired sulphur content in the product is well within the scope of the person skilled in the art of hydroprocessing.

20

THIS PAGE BLANK (USPTO)

ACH 2823 PDEP

12

EPO - DG 1

04. 09. 2000

CLAIMS

1. A process for reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive to a sulphidation step and/or activation step, and contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 500 ppm or less with the optionally sulphided and/or activated catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.
2. The process of claim 1 wherein the sulphur content of the product is less than 50 ppm.
3. The process of claim 1 or 2 wherein the S-containing organic additive is a mercaptocarboxylic acid represented by the general formula HS-R1-COOR, wherein R1 stands for a divalent hydrocarbon group with 1-10 carbon atoms and R stands for a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, or a linear or branched alkyl group having 1 to 10 carbon atoms.
4. A two-step process for converting a starting feedstock having a sulphur content of above 0.1 wt.% into a product having a sulphur content of 200 ppm or less, wherein the process comprises optionally sulphiding and/or activating a first and a second catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive, contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 0.1 wt.% or more with the first catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, with the second catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.

ACH 2823 PDEP

13

5. The process of claim 4 wherein the first catalyst comprises molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, while the second catalyst comprises molybdenum as Group VIB metal component and nickel as Group VIII metal component.

ACH 2823 PDEP

14

EPO - DG 1

04. 09. 2000

ABSTRACT

The present invention pertains to a process for reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm, comprising optionally subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an S-containing organic additive to a sulphidation step and/or activation step, and contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 500 ppm or less with the optionally sulphided and/or activated catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm, preferably less than 50 ppm.

THIS PAGE BLANK (USPTO)